

## DESCRIPTION

## ELECTROPHOTOGRAPHIC PHOTORECEPTOR AND ELECTROPHOTOGRAPH

## Technical Field

[0001]

The present invention relates to an electrophotographic photoreceptor used for  
5 electrophotographic apparatuses such as copying machines, LED, LD printers, etc. and particularly to an electrophotographic photoreceptor which has an undercoat layer and uses an organic photoconductive material, and an electrophotographic apparatus provided  
10 with the photoreceptor.

## Background Art

[0002]

In general, an electrophotographic process using a photoreceptor is performed in the following  
15 manner. That is, the photoreceptor is charged in the dark by a charging roller in the case of, for example, a contact charging method, and then exposed using LED or LD as an imagewise exposing means to selectively dissipate the charge in only the exposed areas to form  
20 an electrostatic latent image, which is rendered visible with a developer to form an image.

Fundamental properties required for the electrophotographic photoreceptors are such functions

that they can be charged to a proper potential in the dark and the surface charge can be dissipated by irradiation with light.

Electrophotographic photoreceptors which are  
5 now put to practical use basically comprise a  
conductive support and a photosensitive layer formed  
thereon. However, these photoreceptors suffer from the  
problems that when an aluminum tube as a conductive  
support is subjected to cutting process by a diamond  
10 cutting tool or the like, cutting oil or powders remain  
on the support and appear as defects at the time of  
formation of images after the photosensitive layer is  
coated on the support or when a high voltage is applied  
to the surface of the photoreceptor, current flows into  
15 the photoreceptor through the defects such as cutting  
burrs and deposited dirt or foreign matters to result  
in partial short-circuits. Furthermore, they appear as  
image defects such as dusts and fogs. Moreover, the  
charge generation layer formed on the conductive  
20 substrate has a thickness of about 1  $\mu\text{m}$ , and is  
influenced by these defects to adversely affect the  
functions as a photoreceptor.

For inhibition of adverse effects caused by  
the defects on the surface of the conductive substrate,  
25 there is usually employed a method of covering the  
defects on the conductive substrate by providing an  
Alumite coat (anodized aluminum coat) on the substrate  
by anodizing treatment or by providing an undercoat

layer using resin materials.

[0003]

However, the Alumite coat has the disadvantages such as inclusion of dirt in the fine pores formed on the surface of the Alumite coat during the formation of the coat and contamination of the surface of the Alumite coat caused at the sealing step of pores or cleaning step. Thus, even if the defects on the surface of the conductive substrate are covered, contamination of the Alumite coat per se adversely affects the photoreceptor.

It is known that resin materials such as polyethylene, polypropylene, polystyrene, acrylic resin, vinyl chloride resin, vinyl acetate resin, polyurethane resin, epoxy resin, silicone resin and polyamide resin are used for the undercoat layer. Of these resins, polyamide resins are particularly preferred.

However, in the case of an electrophotographic photoreceptor in which polyamide resin or the like is used for the undercoat layer, since the volume resistivity of the photoreceptor is about  $10^{12}$ - $10^{15}$   $\Omega\cdot\text{cm}$ , residual potential is accumulated in the photoreceptor unless the undercoat layer is made thin to a thickness of 1  $\mu\text{m}$  or less, and as a result, dusts or fogs occur in the resulting images. On the other hand, if the undercoat layer is made thin, not only the defects on the conductive support cannot be

covered, but also injection of holes from the substrate is accelerated during repeated use to cause considerable reduction of charging potential and decrease of photosensitivity, resulting in formation of  
5 dusts and fogs in the image to damage the image quality.

[0004]

An undercoat layer is proposed which comprises a polyimide resin soluble in an organic  
10 solvent and has a thickness of 0.5  $\mu\text{m}$  (e.g. Patent Document 1).

Patent Document 1: JP-A-8-30007

[0005]

However, it has been found that in the case  
15 of combining the conventional charge transport agent with the undercoat layer comprising a polyimide resin and having a thin thickness of less than 1.0  $\mu\text{m}$  as disclosed in Patent Document 1, the residual potential after repeated use of the photoreceptor increases,  
20 resulting in dusts and fogs in the image.

Furthermore, in the case of the electrophotographic apparatus provided with a contact charging member which applies a charging voltage by directly contacting the undercoat layer with  
25 photoreceptor, a high voltage is directly applied to the electrophotographic photoreceptor, and hence dusts and fogs are often generated.

## Disclosure of Invention

### Problem to be solved by the Invention

[0006]

The object of the present invention is to  
5 provide an electrophotographic photoreceptor which is  
excellent in repetition stability and environmental  
characteristics by covering the defects on the  
conductive substrate without damaging the excellent  
electrophotographic characteristics.

### 10 Means for Solving the Problem

[0007]

As a result of intensive research conducted  
by the inventors in an attempt to solve the above  
problems, it has been found that an electrophotographic  
15 photoreceptor comprising a conductive support and a  
photosensitive layer formed on the conductive support,  
with an undercoat layer provided therebetween, is free  
from the above problems in the conventional  
technologies and maintains excellent electrostatic  
20 characteristics over a long period of time in case the  
undercoat layer contains a specific polyimide resin and  
a specific charge generation agent. Thus, the present  
invention has been accomplished.

[0008]

25 That is, the present invention relates to an  
electrophotographic photoreceptor comprising a  
conductive support and a photosensitive layer formed

thereon, with an undercoat layer provided between the support and the photosensitive layer, characterized in that the undercoat layer contains a polyimide resin and the photosensitive layer contains, as a charge

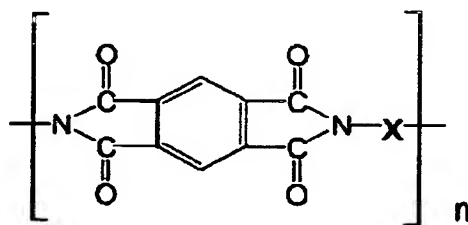
- 5 generation agent, oxytitanium phthalocyanine showing a main diffraction peak intensity at a Bragg angle ( $2\theta \pm 0.2^\circ$ ) of  $27.3^\circ$  in X-ray diffraction spectrum when measured using  $\text{CuK}\alpha$  as a radiation source.

According to the invention described in claim  
10 1 having the above construction, the defects of the conductive support such as pin holes can be covered and furthermore increase of residual potential after repeated use can be inhibited and generation of dusts and fogs on the image can be prevented.

15 [0009]

The invention described in claim 2 relates to an electrophotographic photoreceptor, wherein the undercoat layer contains a polyimide resin represented by the following formula [I].

20 Formula [I]



(in the formula, X is a divalent polycyclic aromatic group in which the aromatic rings may be linked by a hetero-atom and n is an integer which shows a

polymerization degree).

[0010]

According to the invention described in claim  
2 having the above construction, increase of residual  
5 potential after repeated use can be inhibited.

[0011]

The invention described in claim 3 relates to  
an electrophotographic photoreceptor of claim 1,  
wherein the undercoat layer has a thickness of 3.0-  
10 50  $\mu\text{m}$ .

[0012]

According to the invention described in claim  
3 having the above construction, even relatively large  
defects on the conductive support can be covered and  
15 the resulting image is free from defects.

[0013]

The invention described in claim 4 relates to  
an electrophotographic photoreceptor of claim 1,  
wherein the undercoat layer contains titanium oxide,  
20 whereby the permittivity of the undercoat layer can be  
enhanced and dispersibility is also improved.  
Moreover, it is preferred that the weight ratio of the  
polyimide resin and titanium oxide is in the range of  
3:1-1:4.

25 [0014]

The invention described in claim 5 relates to  
an electrophotographic photoreceptor of claim 1,  
wherein the undercoat layer has a two-layer structure

comprising a layer containing a polyimide resin represented by the formula [I] and a layer comprising a thermosetting resin or a thermoplastic resin provided on the layer containing polyimide resin, whereby even  
5 if the undercoat layer is thick, accumulation of the residual potential can be inhibited and chargeability can be stabilized, resulting in improvement in image quality.

[0015]

10           The invention described in claim 6 relates to an electrophotographic photoreceptor of claim 1, wherein a tube which is not subjected to cutting process is used as the conductive support, whereby the defects on the surface of the conductive support can be  
15 surely covered.

[0016]

          The invention described in claim 7 relates to an electrophotographic apparatus using the electrophotographic photoreceptor of claims 1-6,  
20 wherein a contact charging means is provided as a charging means, whereby the object of the present invention can be attained.

[0017]

          The invention described in claim 8 relates to  
25 an electrophotographic apparatus using the electrophotographic photoreceptor of claims 1-6, wherein an exposing means uses a semiconductor laser, whereby the problem of interference fringes in the

image can be solved.

#### Advantages of the Invention

[0018]

In the electrophotographic photoreceptor of  
5 the present invention, electrostatic characteristics  
such as surface potential and potential after exposure  
are not greatly deteriorated even after repeated use,  
no image defects occur and repetition stability is  
high.

10 Therefore, according to the present  
invention, there can be provided an electrophotographic  
photoreceptor which has excellent electrophotographic  
characteristics, cleanability and oil resistance and,  
besides, can be simplified in its maintenance.

15 [0019]

The preferred embodiments of the  
electrophotographic photoreceptor according to the  
present invention will be explained in detail below.

The present invention is applied to, for  
20 example, a double-layered type electrophotographic  
photoreceptor comprising a conductive support, a charge  
generation layer containing at least a charge  
generation agent and formed on the support, and a  
charge transport layer containing at least a charge  
25 transport agent and formed on the charge generation  
layer. In this case, the photosensitive layer is  
formed of the charge generation layer and the charge

transport layer.

Furthermore, the present invention can also be applied to a monolayer type electrophotographic photoreceptor in which the charge generation agent and  
5 the charge transport agent are contained in the same layer or an inversely laminated type electrophotographic photoreceptor in which the charge transport layer is first formed and thereafter the charge generation layer is laminated thereon.

10 [0020]

As the conductive support usable in the present invention, various materials having electrical conductivity can be used with no limitation in the kind and shape thereof, and examples of the materials are  
15 worked pieces of metals or alloys thereof such as aluminum, brass, stainless steel, nickel, chromium, titanium, gold, silver, copper, tin, platinum, molybdenum and indium, plastic sheets or films to which electrical conductivity is imparted by vacuum  
20 deposition or plating of the above metals or conductive materials such carbon, conductive glasses made by coating with tin oxide, indium oxide, aluminum iodide, and the like. As for the shape of the conductive supports, there may be used those which have a shape of  
25 drum, rod, plate, sheet or belt.

Among them, suitable are aluminum alloys of JIS3000 series, JIS5000 series, JIS6000 series, etc., which are shaped by general methods such as EI method,

ED method, DI method, and II method, and preferred are uncut tubes which are not subjected to surface cutting process using a diamond cutting tool or surface treatments such as abrasion and anodizing treatments.

5 [0021]

The charge generation agents usable in the present invention are preferably disazo pigments and oxytitanium phthalocyanine because they have good affinity in sensitivity. Particularly, oxytitanium  
10 phthalocyanine is reported to have many crystal forms, and, among them, especially preferred for the electrophotographic photoreceptor of the present invention is oxytitanium phthalocyanine showing a main diffraction peak intensity at a Bragg angle ( $2\theta \pm 0.2^\circ$ )  
15 of  $27.3^\circ$  in X-ray diffraction spectrum when measured using  $\text{CuK}\alpha$  as a radiation source. The thickness is  $0.01\text{--}5.0\text{ }\mu\text{m}$ , preferably  $0.1\text{--}1.0\text{ }\mu\text{m}$ .

[0022]

The charge generation agent may be used each  
20 alone or in admixture of two or more for obtaining proper light sensitivity wavelength or sensitization action.

[0023]

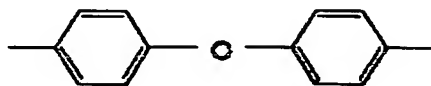
The undercoat layer in the present invention  
25 may contain an intermediate before polyimidation, and the mixing ratio of the polyimide precursor and the polyimide resin is such that the polyimide resin is contained in an amount of suitably 20–70%, preferably

30-50% based on the total weight of the polyimide resin and the polyimide precursor. If the content of the polyimide resin is less than 20%, the undercoat layer dissolves in the organic solvent, and if it is more  
 5 than 70%, the intermediate is in nearly imidated state, resulting in accumulation of residual potential after repeated use and deterioration in image quality.

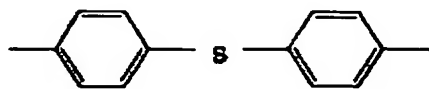
[0024]

The molecular weight of the polyimide resin  
 10 is preferably 1,000-100,000, especially preferably 10,000-30,000. Examples of X in the formula [I] are as follows.

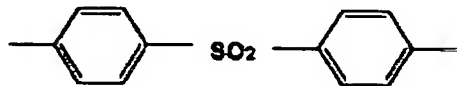
[X-1]



[X-2]



15 [X-3]



[0025]

In the electrophotographic photoreceptor of the present invention comprising a conductive support and a photosensitive layer formed on the support, with

an undercoat layer provided therebetween, the undercoat layer contains a polyimide resin represented by the formula [I] whereby film formability is improved, defects such as pin holes on the conductive support can  
5 be covered even when the layer is thin, and the photosensitive layer is superior in barrier function and adhesion function. The thickness is 3.0-50  $\mu\text{m}$ , preferably 5-30  $\mu\text{m}$ .

[0026]

10 The drying temperature in formation of the undercoat layer is suitably 110-170°C, preferably 130-150°C. If it is lower than 110°C, the undercoat layer dissolves in the solvent and hence cannot be coated on the photoreceptor. If the undercoat layer is dried at  
15 110°C or higher, it does not dissolve in the organic solvent. If the drying temperature is higher than 170°C, the residual potential after repeated use increases to cause change in image density.

[0027]

20 Further, when the undercoat layer has a two-layer structure comprising a layer containing a polyimide resin represented by the formula [I] and a layer comprising a thermosetting resin or a thermoplastic resin provided thereon, even if the  
25 thickness of the undercoat layer increases, the accumulation of residual potential can be inhibited and besides quality of image is improved.

[0028]

In the electrophotographic photoreceptor of the present invention, the undercoat layer may contain titanium oxide. The surface of titanium oxide particles used in the present invention may be  
5 subjected to various treatments so long as they do not reduce volume resistivity. For example, the particle surface can be coated with an oxide film using aluminum, silicon, nickel or the like as a treating agent. In addition, if necessary, water repellency can  
10 be imparted to the particles using a coupling agent or the like. The average particle diameter of the titanium oxide is preferably 1  $\mu\text{m}$  or less, more preferably 0.01-0.5  $\mu\text{m}$ . The content of the titanium oxide is preferably 0.5-4 when the amount of the  
15 polyimide is assumed to be 1.

[0029]

Furthermore, the undercoat layer may have a two-layer structure of a layer comprising a polyimide resin and a layer comprising a thermosetting resin or a  
20 thermoplastic resin provided thereon. As the thermosetting resin, mention may be made of epoxy resin, polyurethane resin, phenolic resin, melamine-alkyd resin, unsaturated polyester resin, etc. As the thermoplastic resin, mention may be made of  
25 styrene-based elastomers, olefin-based elastomers, urethane-based elastomers, polyvinyl chloride-based elastomers, etc. The thickness of the resin layer provided on the polyimide resin layer is 0.1-10.0  $\mu\text{m}$ ,

preferably 0.8-5.0  $\mu\text{m}$ .

[0030]

Both or one of the two layers may contain a white pigment for the purpose of inhibiting interference of light during exposure with semiconductor laser. Examples of the white pigment are titanium oxide, zinc oxide, silica, etc.

[0031]

Binder resins used for the formation of the photosensitive layer include, for example, photosetting resins such as polycarbonate resin, styrene resin, acrylic resin, styrene-acryl resin, ethylene-vinyl acetate resin, polypropylene resin, vinyl chloride resin, chlorinated polyether, vinyl chloride-vinyl acetate resin, polyester resin, furan resin, nitrile resin, alkyd resin, polyacetal resin, polymethylpentene resin, polyamide resin, polyurethane resin, epoxy resin, polyarylate resin, diarylate resin, polysulfone resin, polyether sulfone resin, polyallyl sulfone resin, silicone resin, ketone resin, polyvinyl butyral resin, polyether resin, phenolic resin, EVA (ethylene-vinylacetate copolymer) resin, ACS (acrylonitrile-chlorinated polyethylene-styrene) resin, ABS (acrylonitrile-butadiene-styrene) resin, and epoxy arylate. These may be used each alone or in admixture of two or more. Moreover, when resins differing in molecular weight are used in admixture, hardness and abrasion resistance can be improved, which is more

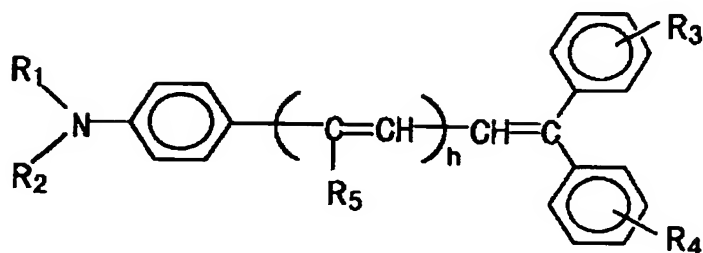
preferred.

[0032]

As the charge transport materials used in the present invention, preferred are compounds shown by the  
5 formulas [II] and/or [III].

[0033]

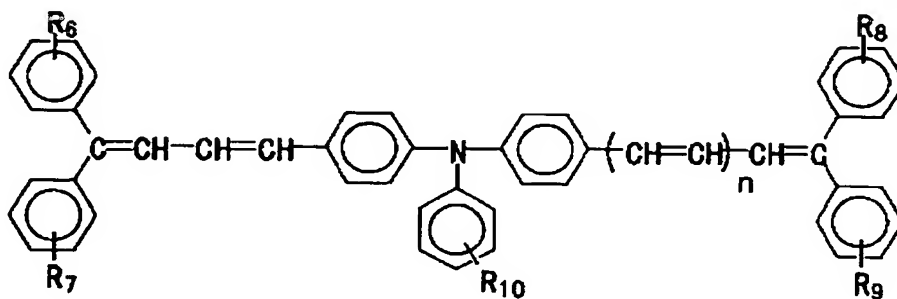
Formula [II]



(in the above formula, R<sub>1</sub>-R<sub>5</sub> independently represent a hydrogen atom, a halogen atom, an alkyl group having 1-  
10 6 carbon atoms which may have a substituent or a substituted or unsubstituted aryl group having 6-12 carbon atoms, and h represents an integer of 0 or 1).

[0034]

Formula [III]

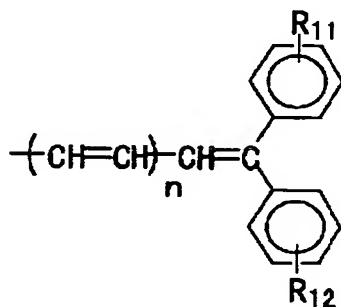


15 (in the above formula, R<sub>6</sub>-R<sub>9</sub> may be the same or

different and independently represent a hydrogen atom,  
 a halogen atom, an alkyl group or alkoxy group having  
 1-6 carbon atoms or an aryl group which may have a  
 substituent,  $R_{10}$  represents a hydrogen atom, a halogen  
 5 atom, an alkyl group or alkoxy group having 1-6 carbon  
 atoms, an aryl group which may have a substituent, an  
 alkenyl group or alkadienyl group which may have a  
 substituent or a group represented by the following  
 formula [IV], and  $n$  represents an integer of 0 or 1).

10 [0035]

Formula [IV]



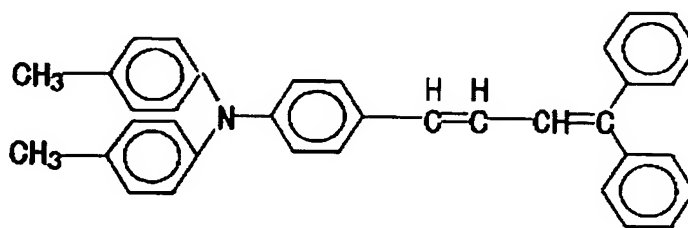
(in the above formula,  $R_{11}$  and  $R_{12}$  may be the same or  
 different and independently represent a hydrogen atom,  
 a halogen atom, an alkyl group or alkoxy group having  
 15 1-6 carbon atoms or an aryl group which may have a  
 substituent, and  $n$  represents an integer of 0 or 1).

The above charge transport materials are high  
 in affinity with oxytitanium phthalocyanine, and the  
 electrophotographic photoreceptor of the present  
 20 invention shows excellent electrical characteristics of  
 high sensitivity and low residual potential.

Among the compounds represented by the formula [II], particularly the compounds represented by the following formulas [V] and [VI] are high in affinity with oxytitanium phthalocyanine and are preferred.

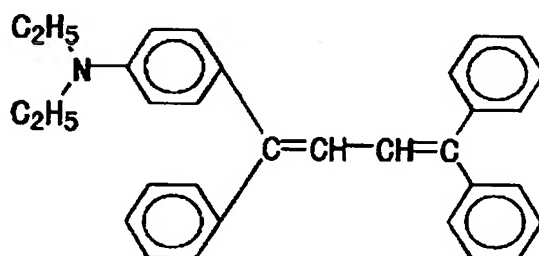
[0036]

Formula [V]



[0037]

Formula [VI]

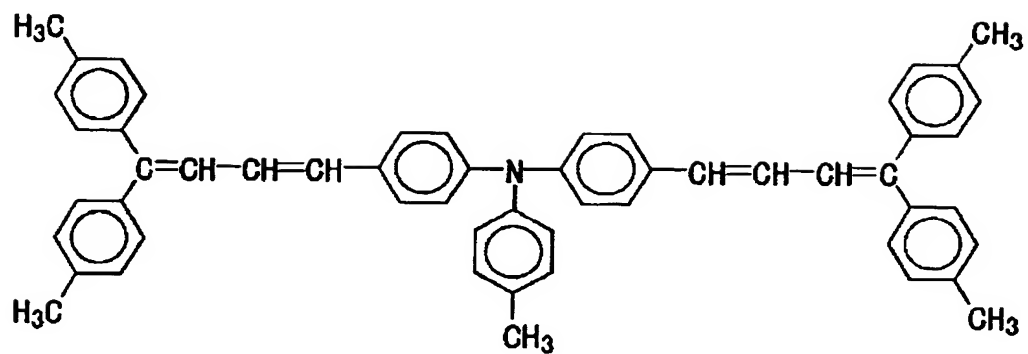


10

Furthermore, among the compounds represented by the formula [III], particularly the compounds represented by the following formulas [VII], [VIII], [IX] and [X] are high in affinity with oxytitanium phthalocyanine and are preferred.

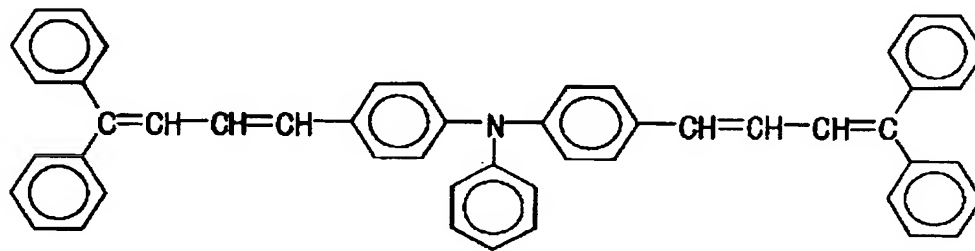
[0038]

Formula [VII]



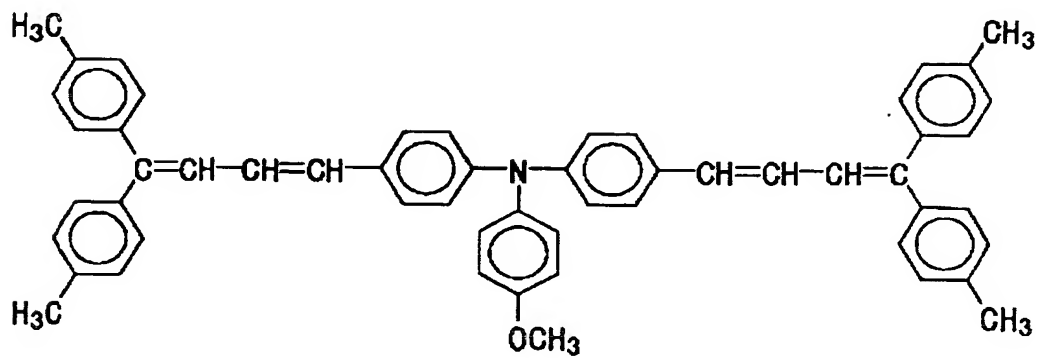
[0039]

Formula [VIII]



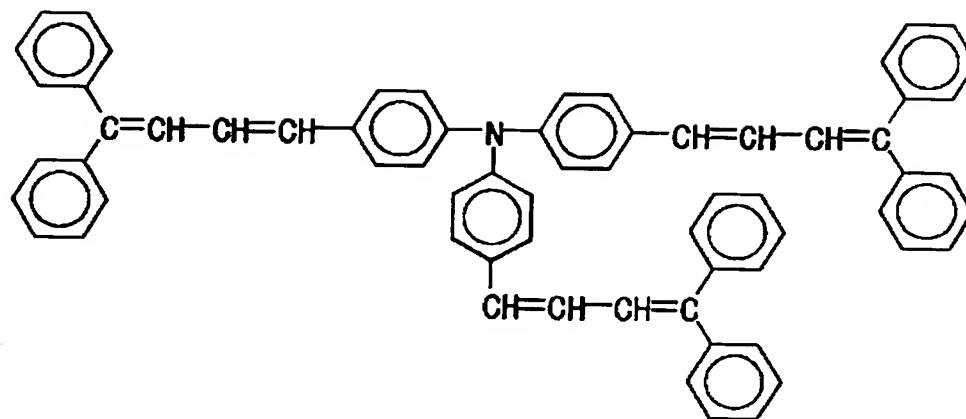
5 [0040]

Formula [IX]



[0041]

Formula [X]



[0042]

When the compound selected from those of the  
 5 formula [II] and the compound selected from those of  
 the formula [III] are used simultaneously as the charge  
 transport materials, good characteristics are also  
 obtained.

[0043]

10 Other charge transport materials than those  
 mentioned above can also be used. The other charge  
 transport materials include polyvinyl carbazole,  
 halogenated polyvinyl carbazole, etc.

Furthermore, other charge transport materials  
 15 can be added to the photosensitive layer of the  
 electrophotographic photoreceptor of the present  
 invention. In this case, the sensitivity of the  
 photosensitive layer can be enhanced or the residual  
 potential can be reduced, and hence the characteristics

of the electrophotographic photoreceptor of the present invention can be improved.

[0044]

As the other charge transport materials which  
5 can be added for improving the characteristics, there  
may be used conductive high molecular compounds such as  
polyvinyl carbazole, halogenated polyvinyl carbazole,  
polyvinylpyrene, polyvinylindoloquinoline,  
polyvinylbenzothiophene, polyvinylanthracene,  
10 polyvinylacridine, polyvinylpyrazoline, polyacetylene,  
polythiophene, polypyrrole, polyphenylene,  
polyphenylenevinylene, polyisothianaphthene,  
polyaniline, polydiacetylene, polyheptadiene,  
polypyridinediyl, polyquinoline, polyphenylene sulfide,  
15 polyferrocenylene, polyperinaphthylene, and  
polyphthalocyanine.

[0045]

Moreover, as the charge transport materials,  
there may also be added low molecular compounds, e.g.,  
20 polycyclic aromatic compounds such as  
trinitrofluorenone, tetracyanoethylene,  
tetracyanoquinodimethane, quinone, diphenquinone,  
naphthoquinone, anthraquinone and derivatives thereof,  
anthracene, pyrene and phenanthrene, nitrogen-  
25 containing heterocyclic compounds such as indole,  
carbazole and imidazole, fluorenone, fluorene,  
oxadiazole, oxazole, pyrazoline, triphenylmethane,  
triphenylamine, enamine, stilbene, other butadiene than

those mentioned above, other hydrazone compounds than those mentioned above, and the like.

[0046]

As charge transport materials used for the similar purpose, there may be added high-molecular solid electrolytes obtained by doping high-molecular compounds such as polyethylene oxide, polypropylene oxide, polyacrylonitrile and polymethacrylic acid with a metal ion such as Li (lithium) ion.

10 [0047]

As additional charge transport materials used for the similar purpose, there may be used organic charge-transfer complexes comprising an electron donor substance and an electron acceptor substance such as tetrathiafurvalene-tetracyanoquinodimethane.

[0048]

The desired photoreceptor characteristics can be obtained by using one charge transport agent or two or more charge transport agents as a mixture. The thickness of the charge transport layer is 5.0-50  $\mu\text{m}$ , preferably 10-30  $\mu\text{m}$ .

In the electrophotographic photoreceptor of the present invention, the total thickness of the photosensitive layer is 10-50  $\mu\text{m}$ , preferably 15-25  $\mu\text{m}$ . For example, in case the undercoat layer is provided in a large thickness of about 25  $\mu\text{m}$ , the charge transport layer may be provided in a thin thickness of about 15  $\mu\text{m}$ . On the other hand, in case the undercoat layer is

provided in a thin thickness of about 1  $\mu\text{m}$ , the charge transport layer may be provided in a large thickness of about 25  $\mu\text{m}$ .

This is because the photoreceptor is required  
5 to have pressure resistance in electrophotographic process using a contact charging means as a charging means. Generally, in the case of a photoreceptor of low pressure resistance, defects occur inside the photoreceptor and on the surface of the photoreceptor  
10 due to leakage of current, and the defects appear as defects of image. That is, since the pressure resistance of the photoreceptor is determined by the total thickness of the photoreceptor, when the undercoat layer is thick, the pressure resistance is  
15 improved and hence the charge transport layer can be made thin.

[0049]

It is preferred for the electrophotographic photoreceptor of the present invention that the  
20 photosensitive layer contains an antioxidant or an ultraviolet absorber for inhibiting change of characteristics and occurrence of cracks caused by oxidative deterioration of photoconductive materials or binder resins and for improving mechanical strength.

25 [0050]

The antioxidants used in the present invention are preferably monophenols such as 2,6-di-tert-butylphenol, 2,6-di-tert-4-methoxyphenol, 2-tert-

butyl-4-methoxyphenol, 2,4-dimethyl-6-tert-butylphenol,  
 2,6-di-tert-butyl-4-methylphenol, butylated  
 hydroxyanisole, stearyl- $\beta$ -(3,5-di-tert-butyl-4-  
 hydroxyphenyl) propionate,  $\alpha$ -tocopherol,  $\beta$ -tocopherol  
 5 and n-octadecyl-3-(3'-5'-di-tert-butyl-4'-  
 hydroxyphenyl) propionate, and polyphenols such as  
 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 4,4'-  
 butylidene-bis-(3-methyl-6-tert-butylphenol), 4,4'-  
 thiobis(6-tert-butyl-3-methylphenol), 1,1,3-tris(2-  
 10 methyl-4-hydroxy-5-tert-butylphenyl)butane, 1,3,5-  
 trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-  
 hydroxybenzyl)benzene and tetrakis[methylene-3(3,5-di-  
 tert-butyl-4-hydroxyphenyl) propionate]methane. These  
 can be contained in the photosensitive layer each alone  
 15 or in combination of two or more.

[0051]

The ultraviolet absorbers are preferably  
 benzotriazole-based absorbers such as 2-(5-methyl-2-  
 hydroxyphenyl)benzotriazole, 2-[2-hydroxy-3,5-bis( $\alpha$ , $\alpha$ -  
 20 dimethylbenzyl)phenyl]-2H-benzotriazole, 2-(3,5-di-  
 tert-butyl-2-hydroxyphenyl)benzotriazole, 2-(3-tert-  
 butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzotriazole,  
 2-(3,5-di-tert-butyl-2-hydroxyphenyl)-5-  
 chlorobenzotriazole, 2-(3,5-di-tert-amyl-2-  
 25 hydroxyphenyl)benzotriazole and 2-(2'-hydroxy-5'-tert-  
 octylphenyl)benzotriazole, and salicylic acid-based  
 absorbers such as phenyl salicylate, p-tert-butylphenyl  
 salicylate and p-octylphenyl salicylate. These can be

contained in the photosensitive layer each alone or in combination of two or more.

[0052]

The antioxidant and the ultraviolet absorber  
5 can be simultaneously added. These can be added to any layer in the photosensitive layer, but it is preferred to add them to the outermost surface layer, particularly, the charge transport layer.

[0053]

10 The amount of the antioxidant added is preferably 3-20% by weight based on the binder resin, and that of the ultraviolet absorber is preferably 3-30% by weight based on the binder resin. When both the antioxidant and the ultraviolet absorber are added  
15 together, the total amount of them is preferably 5-40% by weight based on the binder resin.

[0054]

In addition to the antioxidant and the ultraviolet absorber, there may be added light  
20 stabilizers such as hindered amines and hindered phenols, aging inhibitors such as diphenylamine compounds, surface active agents, etc. to the photosensitive layer.

[0055]

25 The general method for forming the photosensitive layer comprises dispersing or dissolving a given photosensitive material and a given binder resin in a solvent to prepare a coating solution and

coating the solution on a given substrate.

[0056]

The coating solution can be coated, depending on the shape of the substrate or state of the coating solution, by dip coating, curtain flow coating, bar coating, roll coating, ring coating, spin coating, spray coating, etc.

The charge generation layer can also be formed by vacuum deposition method.

10 [0057]

The solvents used for coating solution include, for example, alcohols such as methanol, ethanol, n-propanol, i-propanol, butanol, methyl cellosolve and ethyl cellosolve, saturated aliphatic hydrocarbons such as pentane, hexane, heptane, octane, cyclohexane and cycloheptane, aromatic hydrocarbons such as toluene and xylene, chlorine-containing hydrocarbons such as dichloromethane, dichloroethane, chloroform and chlorobenzene, ethers such as dimethyl ether, diethyl ether and tetrahydrofuran (THF), ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone, esters such as ethyl formate, propyl formate, methyl acetate, ethyl acetate, propyl acetate, butyl acetate and methyl propionate, and amides such as N,N-dimethylformamide, dimethyl sulfoxide and N-methyl-2-pyrrolidone. These may be used each alone or in admixture of two or more.

[0058]

Furthermore, an intermediate layer comprising a resin in which a metal compound, metal oxide, carbon, silica, resin powder or the like is dispersed can be provided on the undercoat layer. Moreover, it may  
5 contain various pigments, electron accepting substances, electron donating substances or the like for improvement of characteristics.

[0059]

In addition, there may be formed a surface  
10 protective layer on the surface of the photosensitive layer by forming an organic thin film of polyvinyl formal resin, polycarbonate resin, fluorocarbon resin, polyurethane resin, silicone resin or the like or a thin film comprising a siloxane structure formed of a  
15 hydrolyzate of silane coupling agent, and, in this case, endurance of the photoreceptor is improved, which is preferred. The surface protective layer may be provided for improving functions other than the endurance.

20 [0060]

Next, the electrophotographic process and electrophotographic apparatus of the present invention will be explained. For the electrophotographic process of the present invention, there may be used known means  
25 such as charging means, exposing means, developing means, transferring means, fixing means and cleaning means. For the charging means, a non-contact charging system such as corona charging system, and a contact

charging system such as charging roller or charging brush can be used. As a light source for imagewise exposing means, there can be used halogen lamp, fluorescent lamp, laser beams, etc. The wavelength of semiconductor laser is 780 nm or less, preferably 780-500 nm, and, in this case, there may be employed such a method as of narrowing down the diameter of laser beam. The developing method includes any of dry developing method, wet developing method, two component developing method, one component developing method, and magnetic/non-magnetic developing method. The transferring means may be either roller or belt.

[0061]

Examples and comparative examples of the electrophotographic photoreceptor according to the present invention will be explained in detail below.

FIG. 1 shows an X-ray diffraction pattern of oxytitanium phthalocyanine which has a main peak at an X-ray diffraction intensity ( $2\theta \pm 0.2^\circ$ )  $27.3^\circ$ .

FIG. 2 shows an X-ray diffraction pattern of a charge generation agent having a maximum peak at an X-ray diffraction intensity of  $7.5^\circ$ .

#### Example 1

[0062]

A mixture comprising titanium oxide particles coated with alumina and a polyimide resin represented by the formula [I] in which X is [X-1] at a weight

ratio of 1:1 was coated on a cylindrical drum of 30 mm in diameter comprising aluminum and subjected to no cutting process, followed by drying at 140°C for 30 minutes to form a first undercoat layer of 18.0  $\mu\text{m}$  in thickness. Then, on the first undercoat layer was coated a coating solution prepared by dissolving a melamine-alkyd resin as a thermosetting resin and titanium oxide at a ratio of 1:3 in methyl ethyl ketone to laminate a second undercoat layer having a thickness of 0.7  $\mu\text{m}$  on the first undercoat layer.

[0063]

Then, thereon was coated a dispersion of oxytitanium phthalocyanine having a main peak at an X-ray diffraction intensity ( $2\theta \pm 0.2^\circ$ )  $27.3^\circ$  (FIG. 1) with using polyvinyl butyral as a binder resin at a thickness of 0.1  $\mu\text{m}$  by dip coating to form a charge generation layer.

[0064]

Then, a coating solution was prepared by dissolving in chloroform a polycarbonate copolymer as a binder resin, a butadiene compound of the formula [VI] as a charge transport agent and 2,6-di-tert-butyl-4-methylphenol as an antioxidant at a weight ratio of polycarbonate copolymer/butadiene compound/2,6-di-tert-butyl-4-methylphenol = 1.0/0.8/0.18.

[0065]

The resulting coating solution was coated by dip coating, followed by drying at 100°C for 1 hour to

form a charge transport layer of 20  $\mu\text{m}$  in thickness,  
thereby obtaining an electrophotographic photoreceptor.

Example 2

[0066]

5           An electrophotographic photoreceptor was  
prepared in the same manner as in Example 1, except  
that the weight ratio of polyimide resin and titanium  
oxide in the first undercoat layer was changed to 2:1.

Example 3

10 [0067]

          An electrophotographic photoreceptor was  
prepared in the same manner as in Example 1, except  
that the weight ratio of polyimide resin and titanium  
oxide in the first undercoat layer was changed to 1:4.

15 Example 4

[0068]

          An electrophotographic photoreceptor was  
prepared in the same manner as in Example 1, except  
that the thickness of the first undercoat layer was  
20 changed to 3.0  $\mu\text{m}$ .

Example 5

[0069]

          An electrophotographic photoreceptor was  
prepared in the same manner as in Example 1, except

that the thickness of the first undercoat layer was changed to 5.0  $\mu\text{m}$ .

Example 6

[0070]

- 5           An electrophotographic photoreceptor was prepared in the same manner as in Example 1, except that the thickness of the first undercoat layer was changed to 13.0  $\mu\text{m}$ .

Example 7

10 [0071]

          An electrophotographic photoreceptor was prepared in the same manner as in Example 1, except that the thickness of the first undercoat layer was changed to 30.0  $\mu\text{m}$ .

15 Example 8

[0072]

- An electrophotographic photoreceptor was prepared in the same manner as in Example 1, except that the thickness of the first undercoat layer was  
20 changed to 50.0  $\mu\text{m}$ .

Example 9

[0073]

          An electrophotographic photoreceptor was prepared in the same manner as in Example 1, except

that the second undercoat layer was omitted.

Example 10

[0074]

5 An electrophotographic photoreceptor was prepared in the same manner as in Example 1, except that the charge transport agent of the formula [VI] used was changed to that of the formula [VII].

Example 11

[0075]

10 An electrophotographic photoreceptor was prepared in the same manner as in Example 1, except that the thickness of the first undercoat layer was changed to 2.0  $\mu\text{m}$ .

Example 12

15 [0076]

An electrophotographic photoreceptor was prepared in the same manner as in Example 1, except that the charge transport agent of the formula [VI] used was changed to that of the formula [V].

20 Comparative Example 1

[0077]

An electrophotographic photoreceptor was prepared in the same manner as in Example 1, except that the charge generation agent used was changed to a

charge generation agent having a maximum peak at an X-ray diffraction intensity  $7.5^{\circ}$ .

Comparative Example 2

[0078]

- 5           An electrophotographic photoreceptor was prepared in the same manner as in Example 1, except that an Alumite layer was formed by anodizing treatment in place of the undercoat layer formed in Example.

Comparative Example 3

10 [0079]

          An electrophotographic photoreceptor was prepared in the same manner as in Example 1, except that the first undercoat layer was omitted.

Comparative Example 4

15 [0080]

          An electrophotographic photoreceptor was prepared in the same manner as in Example 1, except that the first undercoat layer and the second undercoat layer were omitted.

20 Comparative Example 5

[0081]

          An electrophotographic photoreceptor was prepared in the same manner as in Example 1, except that a bisazo compound was used in place of the charge

generation agent used in Example 1.

[0082]

Evaluation method

[Measurement of electrostatic characteristics, repeated  
5 cycling test, image test]

The cylindrical electrophotographic photoreceptors prepared in Examples 1-12 and Comparative Examples 1-5 were charged using a direct charging type Microline 14 printer manufactured by Oki  
10 Data Co., Ltd. in an environment of normal temperature and humidity (24°C, 40% RH) so that the photoreceptors after charged had a surface potential of -800 V, and were subjected to initial setting so that the photoreceptors after exposed by LED had a surface  
15 potential of -50 V. Then, after printing of 20,000 copies of A4 size, the surface potential  $V_0$  (-V) and the residual potential  $V_R$  (-V) were measured. The image test was conducted by evaluating the images after continuous printing of 20,000 copies. The results are  
20 shown in Table 1. In Table 1, the mark "O" means that the resulting image was good in quality and "X" means that the resulting image was defective and practically unacceptable.

[0083]

[Table 1]

	After printing of 20,000 copies		Image after printing of 20,000 copies				
	Surface potential (-V)	Potential after exposure (-V)	Leakage	Transfer memory	Dusts, fogs	Reduction of density	Black points
Example 1	800	65	O	O	O	O	O
Example 2	795	63	O	O	O	O	O
Example 3	795	63	O	O	O	O	O
Example 4	790	60	O	O	O	O	O
Example 5	795	62	O	O	O	O	O
Example 6	795	63	O	O	O	O	O
Example 7	795	66	O	O	O	O	O
Example 8	800	66	O	O	O	O	O
Example 9	770	57	O	O	O	O	O
Example 10	795	57	O	O	O	O	O
Example 11	800	57	O	O	O	O	O
Example 12	800	68	O	O	O	O	O
Comparative Example 1	780	56	O	X	O	O	O
Comparative Example 2	780	56	O	X	O	X	O
Comparative Example 3	760	50	X	X	X	O	X
Comparative Example 4	755	50	X	X	X	O	X
Comparative Example 5	750	50	O	X	X	O	O

[0084]

As is clear from Table 1, the electrophotographic photoreceptors of Examples 1-12 were satisfactory in chargeability and less in light-  
5 induced fatigue even after repeated printing of 20,000 copies, and, furthermore, there occurred no defects in the resulting images such as dusts and fogs.

[0085]

In addition, good results were also obtained  
10 when titanium oxide was added to the polyimide resin or thermosetting resin or thermoplastic resin was laminated on the polyimide resin layer.

That is, the results were particularly superior in Examples 1-12.

15 [0086]

On the other hand, in case the polyimide resin layer was not present in Comparative Examples 3 and 4, black points due to transfer memory and dusts and fogs occurred.

20

#### Brief Description of Drawings

[0087]

FIG. 1 is an X-ray diffraction pattern of oxytitanium phthalocyanine having a main peak at an X-  
25 ray diffraction intensity ( $2\theta \pm 0.2^\circ$ )  $27.3^\circ$ .

FIG. 2 is an X-ray diffraction pattern of a charge generating agent having a maximum peak at an X-ray diffraction intensity  $7.5^\circ$ .